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THE ELECTROCATALYTIC REDUCTION OF CARBON DIOXIDE USING MACROCYC--ETC(U)

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The Electrocatalytic Reduction of Carbon Dioxide
Using Macrocycles of Nickel and Cobalt

by

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20. g.c. analysis. The solvents used were either $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ or water only. Carbon monoxide was found to comprise at least 50% of the total reduced products in all cases; H_2 was also produced in most cases. While a protic source was found to be necessary for CO_2 reduction to occur, the results show that CO_2 competes effectively with H^+ for the electrons available from the electrochemically reduced metal complexes. In addition, the reduction was found to be electrocatalytic, with current efficiencies for total reduced products as high as 98%.

The Electrocatalytic Reduction of Carbon Dioxide
Using Macrocycles of Nickel and Cobalt

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Abstract

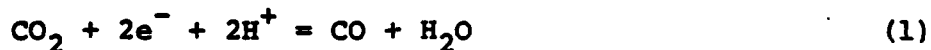
Carbon dioxide has been activated towards reduction by electrochemically primed transition metal complexes. This indirect reduction allows more favorable electrode potentials than those required when CO₂ is reduced directly. The metal complexes employed were Curtis type tetraazamacrocyclic complexes of nickel and cobalt. The electrode potentials ranged from -1.3v to -1.6v vs SCE. Evidence for CO₂ reduction was obtained from controlled potential coulometry experiments performed in a gas tight electrolysis cell followed by g.c. analysis. The solvents used were either CH₃CN-H₂O or water only. Carbon monoxide was found to comprise at least 50% of the total reduced products in all cases; H₂ was also produced in most cases. While a protic source was found to be necessary for CO₂ reduction to occur, the results show that CO₂ competes effectively with H⁺ for the electrons available from the electrochemically reduced metal complexes. In addition, the reduction was found to be electrocatalytic, with current efficiencies for total reduced products as high as 98%.

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Sir:

The reduction of carbon dioxide, this planet's most abundant source of carbon, is an important objective in the development of alternative fuel sources. This reduction requires both the action of a catalyst and energy input to be viable. The former is a result of the large overpotential associated with the direct electrochemical reduction of CO_2 , while the latter results from the fact that CO_2 is the stable carbon end product of metabolism and other combustions. Equation (1) shows the half-cell reaction for the two electron reduction of CO_2 to CO . The standard potential for this reaction is -0.10v while at pH 7 the potential becomes -0.52v .



The direct electroreduction of CO_2 on various metal electrodes in both aqueous and nonaqueous media has been reported by numerous authors.¹⁻⁴ However, these direct electroreductions have required potentials more negative than ca -2v vs SCE. In this paper we describe an indirect electrochemical reduction of CO_2 which involves the initial reduction of metal complexes and their subsequent reaction with CO_2 . This approach facilitates reducing CO_2 at potentials closer to the thermodynamic values. The metal complexes are thus redox activated catalysts.

The catalysts employed were the tetraazamacrocyclic complexes(1-5) of cobalt and nickel. These are listed in Table I, along with the cell potentials applied during the electrocatalytic reactions. The preparation and electrochemical behavior of these complexes in nonaqueous solvents has been previously reported.⁵ Each complex

undergoes uncomplicated reversible or quasireversible one electron transfers in dry, nonaqueous solvents. Evidence for CO₂ reduction was obtained from controlled potential coulometry (cpc) experiments performed in a gas tight electrolysis cell under an exclusively carbon dioxide atmosphere.⁶ The concentration of catalyst ranged from 1mM to 2.5mM in these experiments, and the solvent systems used were either acetonitrile/water or water only. Gas chromatographic analysis was used to determine the composition of the gases above the electrolysis solution during and after each run.⁷ Formate was analyzed for either by esterification to methyl formate or by dehydration to CO, each followed by g.c. analysis. In a typical run, 9×10^{-5} moles of 2 in 75 mL of acetonitrile/water (1:2 v/v) was electrolyzed under CO₂ at ambient room temperature. After 1.1 hours, 82 coulombs had been passed, corresponding to $8 e^-$ per cobalt complex, and g.c. analysis revealed 1.8×10^{-4} moles of CO and 1.8×10^{-4} moles of H₂ as the only products, corresponding to a current efficiency of 94%.

The results for these electrolysis experiments, which were each performed at least six times, are shown in Table I. Compounds 1, 2, and 3 display current efficiencies of greater than 90% and rates of catalysis in terms of electrons passed per complex per hour ranging from 2 to 9 at ambient room temperature. Longer term electrolyses performed with complexes 1 and 2 underscore the catalytic nature of the observed reactions. For example, an electrolysis using 8.8×10^{-5} moles of complex 2 produced 5.1×10^{-3} moles of H₂ and 1.4×10^{-3} moles of CO after 19 hours of electrolysis under a CO₂ atmosphere, corresponding to 164 turnovers or electrons passed

per catalyst complex, and a current efficiency of 96%. Similar results were obtained from other runs using both 1 and 2.

The nature of the catalytic reduction process was investigated further by several additional cpc experiments, the results of which are summarized as follows: (1) No carbon monoxide was detected when electrolyses were performed under a CO_2 atmosphere at potentials as negative as -1.6 V. vs SCE in the absence of the catalysts. (2) No carbon monoxide was detected when complexes 1, 2, or 4 were electrolyzed in dry DMSO in the presence of CO_2 . However, when water was added to the closed cell containing one of the M^+ species generated under these conditions, both CO and H_2 were formed, and catalytic activity under electrolysis began. (3) No carbon monoxide was detected when complexes 2 or 3 were electrolyzed under Ar or N_2 . When these complexes were electrolyzed in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture under N_2 , the only product formed was molecular hydrogen with current efficiencies as high as 80% for complex 2. The rate of H_2 production in these electrolyses was approximately the same as the rate of $\text{CO} + \text{H}_2$ production when the complexes were electrolyzed under a carbon dioxide atmosphere. (4) No carbon dioxide was detected when either complex 1 or 2 was electrolyzed under an exclusively CO atmosphere, even after several hours, and no H_2 was produced in the absence of electrolysis under a CO atmosphere. Thus the possibility of H_2 production via the water gas shift reaction under these conditions was eliminated. An ir solution spectrum of complex 1 which had been electrolyzed under CO exhibited ν_{CO} at ca 1900 cm^{-1} which was removed upon flushing the solution with Ar. (5) No carbon monoxide was detected after the direct

interaction of H_2 with CO_2 in the absence or presence of the complexes listed in Table I. (6) Trace amounts of formate were detected in catalytic runs using compounds 2 and 4. However, formate was not stable under the conditions generated during the electrolyses. When formate was added to an electrolysis of complex 2 under N_2 , a stoichiometric amount of CO_2 was produced based on moles of catalyst. (7) The rate of catalysis was increased significantly by an increase in temperature. For catalyst 1 (1.2mM solution) electrolyzed at $40^\circ C$, the rate of catalysis increased to 22 turnovers per hour. (8) Cyclic voltammograms and IR spectra were taken of compounds 1, 2, 3 and 4 isolated at the end of several runs. These were identical with CV's and IR's of the original compounds.

From these results, a number of conclusions can be drawn. First and foremost, an indirect electrochemical reduction of CO_2 has been accomplished at potentials between -1.3 and -1.6 v vs SCE. The reduction is catalytic in metal complex, with activity not decreasing for periods as long as 24 hrs. In most cases, the catalyst was isolated at the end of the run in its original form. A protic source is also needed for the production of CO and H_2 ; in its absence, simple stoichiometric reduction of the complex is observed.





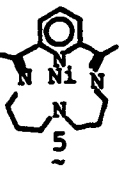
While detailed mechanistic information is still lacking, the fact that CO and H_2 are the major reduction products and that they occur only when a protic source is present suggests that both products may arise from a common intermediate which is most likely a metal hydride. Since the rate of H_2 production under N_2 is

similar to the rate of $\text{CO} + \text{H}_2$ production under CO_2 , it appears that CO_2 is competing effectively with protons for the reducing electrons in these systems. This is indeed encouraging since CO_2 has much poorer ligating abilities than does H^+ . The intimate reduction of CO_2 may therefore proceed via direct attack of CO_2 on the proposed hydride species, obviating the necessity of its prior coordination at the metal center. Studies designed to confirm this hypothesis, and to improve the catalysis are under way.

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	Electrode Potential vs SCE ^a	Average Current Efficiency ^b	Products (ratio) ^c	Turnovers Per Hour at 23°C ^d	Solvent System
 1	2+ -1.6	93%	CO H ₂ 1 : 1	7.8	.1M KNO ₃ in H ₂ O/CH ₃ CN 2:1 (v/v) or H ₂ O only
 2	2+ -1.5	90%	CO H ₂ 1 : 1	9	.1M KNO ₃ in H ₂ O/CH ₃ CN 2:1 (v/v) or H ₂ O only
 3	2+ -1.6	98%	CO H ₂ 2 : 1	6	.1M LiClO ₄ in H ₂ O/CH ₃ CN 2:1 (v/v)
 4	2+ -1.5	—	e	—	
 5	2+ -1.3	44%	CO	2.1	.1M KNO ₃ in H ₂ O/CH ₃ CN 2:1 (v/v)

- All CPC experiments were carried out at the cathodic $E_{1/2}$ or .1 volts more negative than the $E_{p,c}$ for the $M^{+2/+1}$ couple in the solvent system used.
- Averaged over numerous runs using the following catalyst concentrations: compounds 1,2,3 and 4 - 1.2mM; compound 5 - 2.5mM.
- See footnote 5.
- Turnovers per hour per mole of catalyst for runs in which the catalyst concentration was 2.4 - 2.4mM. A turnover is defined as one equivalent of electrons passed through the electrolysis cell per mole of catalyst. Since the reduction products require two electrons for their formation, these numbers correspond to twice the moles of product formed per mole of complex per hour.
- Although catalysis has been observed using this compound in a number of solvent systems, reliable current efficiencies and rates have not been obtained.

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6. The gas tight cell was a 250 mL three neck 14/20 round bottom flask equipped with two side arms. The working electrode in all the experiments was mercury. The connection to the Hg was made through a Pt wire inserted through the bottom of the flask. The cell volume was 270 mL of which 185 mL were occupied by gases.
7. Molecular hydrogen and carbon monoxide were determined on a 2' X 1/4" column of molecular sieves 5A and a 12' X 1/4" column of PoropakQ at 43°C; Carbon dioxide was determined on the Poropak column under the same conditions.
8. Turnover numbers are calculated from the moles of electrons passed per mole of catalyst. Current efficiencies are calculated from the ratio of moles of product detected to the moles of product expected on the basis of a two electron reduction of CO₂ and the measured number of coulombs passed during the run.

